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ON THE MOLECULAR CONDUCTIVITY OF DYESTUFFS IN SOLUTION AND THE INFLUENCE OF FOREIGN SUBSTANCE ON THE SAME*

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ABSTRACT. The paper describes the results of the measurements of the molecular conductivities of dyestuffs in solution. It has been found that in most of the cases the molecular conductivities of dyestuffs in solution do not have linear relations with square root of concentration. The departure of the conductivity curve from the perfect straight line has been explained as due to the formation of ionic micelles. The influence of foreign molecule or ions on the conductivity of the fluorescent dyestuffs in solution has been investigated as well.

INTRODUCTION

The quenching of fluorescence of dyestuffs with increase in concentrations or by addition of salts has been explained by various workers as due to two causes : (1) quenching by deactivating collisions of the second kind, (2) the formation of associated molecules which themselves are non-fluorescent and have a somewhat modified absorption spectrum.

The diminished fluorescence in concentrated dye solutions is largely due to aggregate formation as shown by the fact that they do not obey Beer's law (1935) as well as by other observations on mean life and depolarisation (Banow, 1929, 1930, 1933). Mitra, (1938) observed a close parallel between the change of molar absorption co-efficients with concentrations and the change of fluorescence yields. It is interesting to note that in very dilute solutions where Beer's law seems to hold, the fluorescence yield remains constant. Further increase in concentration diminishes the yield as well as absorption capacity per molecule. It is difficult to explain on purely collisional hypothesis the change of the absorption co-efficients to the extent observed by Mitra. Lewschin (1927) found modified absorption spectra of dyestuffs. He studied the effect of temperature on specific fluorescent capacity in concentrated solutions. Though temperature increases the number of collisions, the fluorescence yield increases at the same rate. Boutaric (1936) has confirmed the above observations which go against the collision of the second kind as means of quenching. Banow (1933) has further shown that increase of temperature has, sometimes, a decreasing effect on the quenching of fluorescence by salts. All these go against the theory of the collision of the second kind and we are thus inclined to look for the explanation in the micelle formation of the ions of the dyestuffs to which the greater part of the effect may be due. The present investigation has been carried out to gain some insight as to the mechanism of micelle formation and to the ionic states of the dyemolecules.

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The mechanism of micelle formation can be best studied from measurements on conductivity of dyestuffs. It is a well known fact that the equivalent conductivity of an electrolyte generally increases with dilution and tends to a limiting value at infinite dilution. It was pointed out by McBain (1913) that the equivalent conductivity of an electrolyte would be increased by the aggregations of ions of one kind to form ionic micelles and the remarkable increase of equivalent conductivity with increasing concentration has been attributed to association of solute molecules. Robinson (1934) and his co-workers determined the transport number as well as the equivalent conductivities of some of the rigorously purified dyestuffs. The equivalent conductivities of dye solutions, when plotted against square root of concentrations, give curves similar in nature to those obtained by Howell and Robinson (1933). The departure of the conductivity curve from the perfect straight line can only be explained on the assumption that ionic micelles are formed with increase in concentration.

The measurement of conductivity of dyes is, however, beset with difficulties. The Kohlrausch method of determining resistances of electrolytes is generally employed using electrodes coated with platinum black. The platinum black coating eliminates the disturbing effect of polarisation but it has certain inherent disadvantages. It adsorbs the solute molecules and acts as catalyst in the oxidation of certain substances, particularly dyestuffs. In our observations the coating has, therefore, been avoided altogether and a method devised by the senior author (Chaudhuri, 1948) to measure electrolytic resistance using bright platinum electrodes has been used. The method gives quite satisfactory results.

EXPERIMENTAL

The arrangement of apparatus is shown in figure 1. It is the usual Wheatstone's bridge arrangement in which an amplifier is used in the galvanometer or telephone arm. The detecting instrument is the vertical wattmeter devised by Mukherjee (1930, 1938). This instrument is composed of two systems of coils of which the fixed system produces the magnetic field and the moving system is deflected by the field. The former is put in the battery arm of the

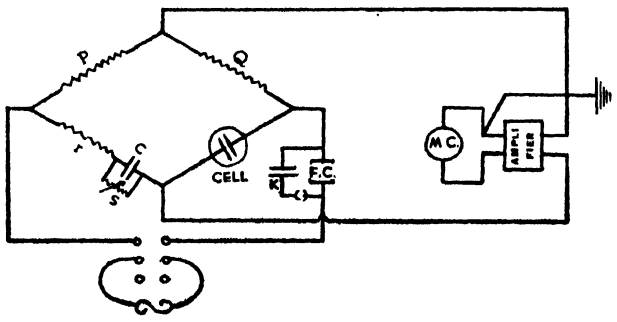

FIG. 1

bridge and the latter in the out-put side of the amplifier. The ratio arms are of equal resistances so that their inductances are

also the same. In the third arm, there is, in series with a resistance r, a condenser C shunted by a variable resistance S. The effective resistance and reactance of the system composed of the condenser and the shunt are respectively

$\frac{S}{1 + S^2C^2p^2}$ and $\frac{S^2Cp}{1 + S^2C^2p^2}$, where $p = 2\pi$ times the frequency of the source.

In the fourth arm is placed the electrolytic cell which can be regarded as consisting of electrolytic resistance, polarisation capacitance and polarisation resistance. The polarisation capacitance is due to the reversible transformation of electrical energy into chemical energy and which is equivalent to an electrostatic condenser. The polarisation resistance is, according to Wien, due to irreversible process at the electrode. Perhaps much of the electrode loss is due to the employment of voltage higher than the decomposition voltage of the solution and was not appreciable in the work of the author. The peak voltage across the electrodes was less than the decomposition voltage of the solution. The electrode resistance ΔR, can, therefore, be made to play insignificant part on the resistance of the solution. The polarisation capacitance can be compensated by introducing a capacitative reactance in the adjacent arm of the bridge. Therefore, when the true balance is obtained with the detecting instrument, the resistance of the third arm, namely,

$$r + \frac{S}{1 + S^2C^2p^2}$$

becomes equal to the resistance of the solution and the reactance $-\frac{S^2Cp}{1 + S^2C^2p^2}$ balances the polarisation reactance of the solution as well as the residual inductive reactance of the third arm.

METHOD OF FINDING THE BALANCE POINT

In detecting instruments of the wattmeter or dynamometer type, the deflection is given by

$$\delta = A\, I_f\, I_m \cos\psi$$

where I_f, I_m are the r.m.s currents in the fixed coils and moving coils respectively and ψ, the phase-difference between them. The deflection is, therefore, zero when

(1) I_f or $I_m = 0$

or (2) $\cos\psi = 0$ *i.e.*, $\psi = \pi/2$

The balance corresponding to condition (1) is called the true balance. In practice, the null point corresponding to condition (2) is easily obtained. If, however, the phase of the current through the fixed coil with respect to the current through the moving coil is altered by introducing a condenser, K, in parallel with the fixed coil, the null point is disturbed and there is deflection one way or the other according as I_f is in advance of, or behind, I_m.

The procedure for finding true balance, is as follows : keeping $s = 0$, a null point is obtained by adjusting r, when the condenser K is off the circuit. Then the direction and extent of deflection are observed when K is introduced. The shunt is then given an arbitrary value and after obtaining the null-piont by adjusting r with K off, the direction and extent of deflection are again observed with K on. Proceeding in this manner a condition is attained when null point will not be disturbed by introducing K. This condition corresponds to true balance.

Determination of Cp: Since the resistance of the solution is equal to $r + \frac{S}{1 + S^2C^2p^2}$ it is necessary to find the value of Cp. A method for determining C_p has been described by Mukherjee (1938). In it the moving coil of the wattmeter is made non-inductive by Sumpner's compensation method and from the null-point corresponding to $\psi = \pi/2$, the value of Cp is found with the aid of the formula :

$$\frac{1}{C^2p^2} = \frac{Q}{P}R\left\{R + \frac{(P+Q)G}{P+Q+G}\right\}$$

Figure 2 shows the arrangement of apparatus.

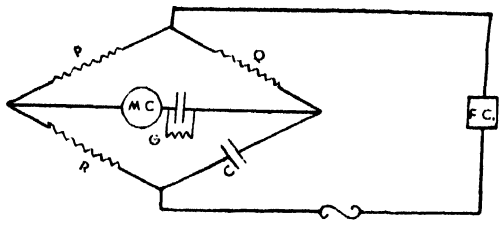

FIG. 2

EXPERIMENTAL RESULTS

In the actual experiment the temperature was kept constant within 1/500th of a degree with a specially designed thermostat and a source producing high audio-frequency alternating current was employed to reduce polarisation effects to a minimum. The amplifier used was a simple resistance-capacity coupled one in which anode resistances attached to the valves were much larger than the valve resistances, thus ensuring the straight line character of the characteristic curves within a long range of grid voltages and eliminating the possibility of a feed-back effect. The output current from the amplifier was obtained through a $4\mu F$ condenser. The amplification was such as to give one ampere (output) current per volt (input).

It took the cell about 2 to 3 hours to come to a steady temperature. The conductivities of different dyestuffs in water and alcoholic solutions at different concentrations were measured at constant temperature. The results of our measurements are given in the accompanying tables and graphs.

TABLE 1

Eosine in water

Molecular concentration C	$\sqrt{C}$	Sp. conductivity	Molecular conductivity
.02792	.167	.007244	259.4
.01396	.117	.003286	235.0
.00698	.0835	.001442	201.6
.00349	.0590	.0006709	192.0
.001745	.0417	.0003432	196.3
.000872	.0290	.0001751	200.6
.000436	.0208	.00009107	208.7
.000218	.0147	.00004968	231.4
.000109	.0104	.00002800	256.7
.0000545	.0074	.00001646	301.8

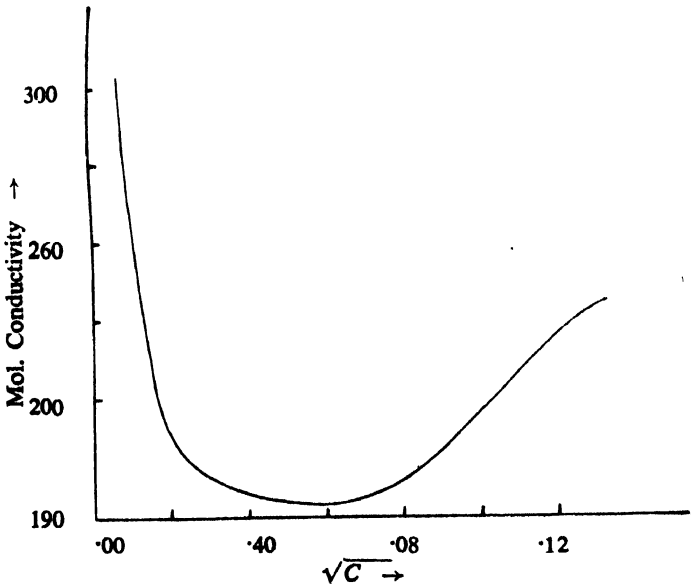

FIG. 3

Eosine in water

TABLE II
Erythrosine in water

Molecular concentration C	$\sqrt{C}$	Sp. conductivity	Molecular conductivity
.005308	.07285	.0006710	126.4
.002654	.05152	.0003375	127.2
.001062	.03259	.0001389	130.8
.0005308	.02304	.00007389	139.2
.0002654	.01629	.00003970	149.6
.0001327	.01152	.00002040	153.7
.00006635	.008145	.00001042	157.0

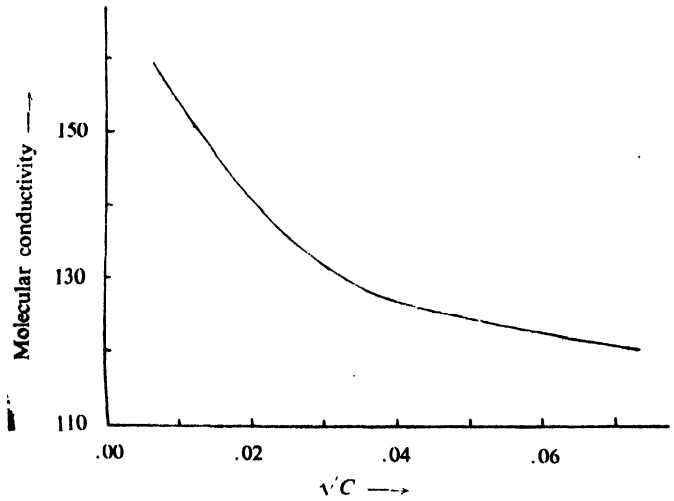

FIG. 4
Erythrosine in water

TABLE III
Methyl violet in water

Molecular concentration C	$\sqrt{C}$	Sp. conductivity	Molecular conductivity
.001271	.0356	.0001021	80.35
.000635	.0252	.00005526	86.98
.0001271	.01127	.00001604	126.20
.0000635	.00797	.00001225	192.80
.00003175	.00563	.00001041	327.30

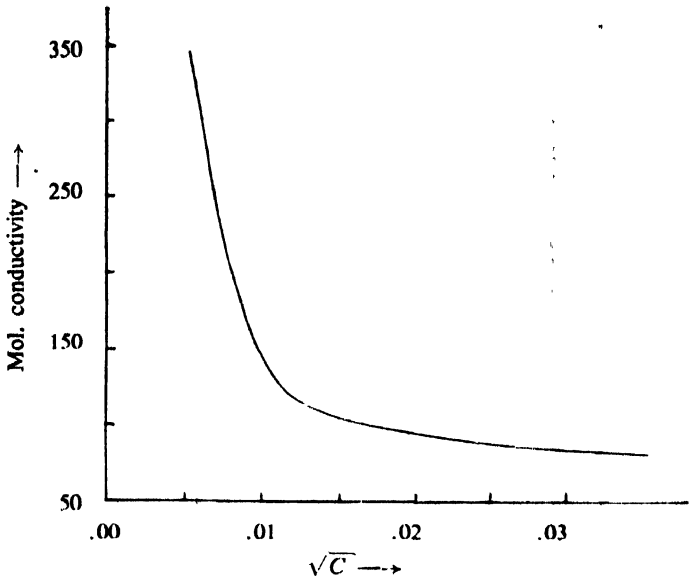

FIG. 5
Methyl violet in water

TABLE IV

Cyanine in water

Molecular concentration C	$\sqrt{C}$	Sp. conductivity	Molecular conductivity
.0001859	.0137	.00002653	142.7
.0000465	.0068	.00001128	201.8
.00002325	.0048	.000008680	386.7
.00001162	.0034	.000007773	693.7
.00000581	.0024	.000007031	1227.0

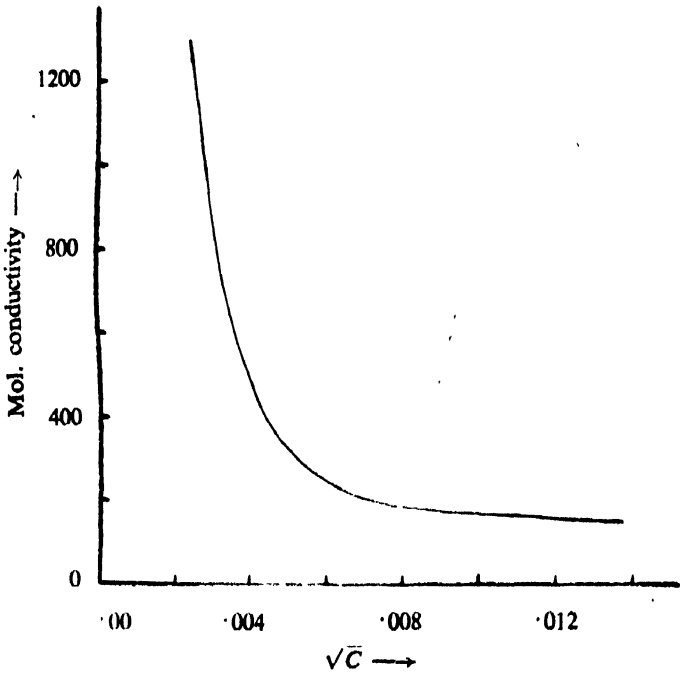

FIG. 6
Cyanine in water

TABLE V

Erythrosine in alcohol

Molecular concentration C	$\sqrt{C}$	Sp. conductivity	Molecular conductivity
.01752	.1324	.00008843	5.048
.008760	.09359	.00005048	5.762
.003480	.06618	.00003027	6.910
.001752	.04185	.00001499	8.557
.000584	.02417	.00000633	10.840
.000292	.01709	.00000395	13.530

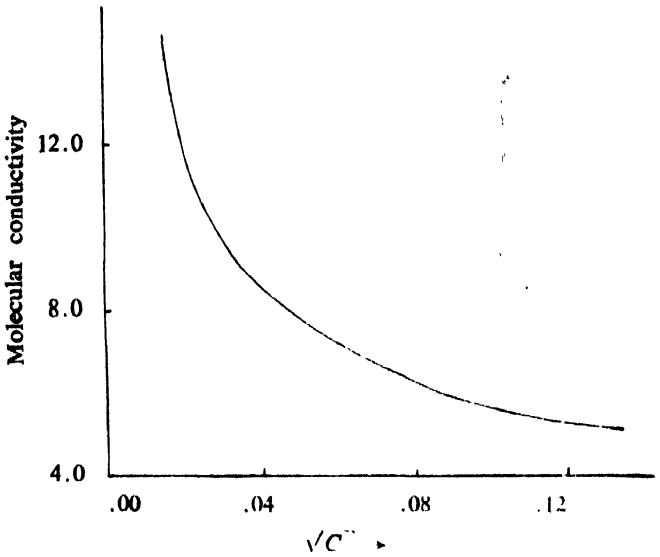

FIG. 7

Erythrosine in alcohol

TABLE VI

Cyanine in alcohol

Molecular concentration C	$\sqrt{C}$	Sp. conductivity	Molecular conductivity
.02324	.152	.0003845	165.5
.00581	.076	.0001236	211.7
.002905	.054	.00007532	259.2
.001452	.038	.00004055	278.9
.000242	.016	.000009406	388.6

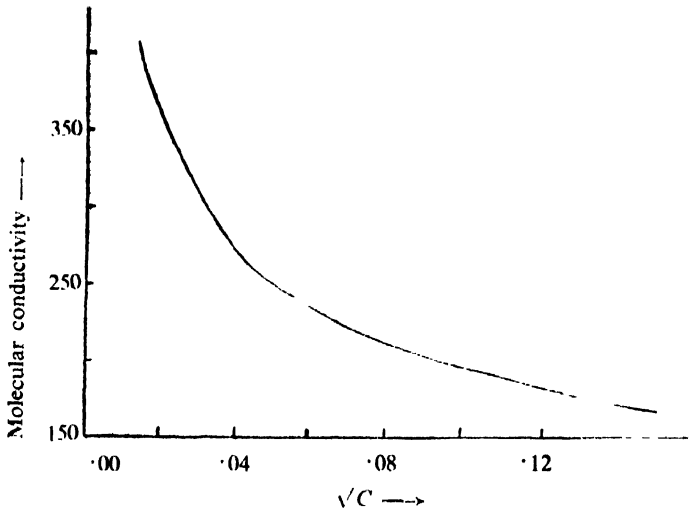

FIG. 8
Cyanine in alcohol

DISCUSSION OF THE RESULTS

It appears from the tables and graphs that the molecular conductivities of dyestuffs in aqueous solution do not have linear relation with square root of concentration. The molecular conductivities, when plotted against square root of concentration, give curves in most of the cases similar to those obtained by Howell and Robinson (1936). Howell and Robinson have worked on the electrical conductivities of aqueous solutions of sodium dodecyl sulphate and sodium hexadecyl sulphate and have found that the curves of the electrical conductivity against the square root of the concentration consist of three well defined sections. Over the first range the fall in conductivity is linear as for a simple electrolyte and is of the same order of magnitude. At the point where the first range is abruptly succeeded by the second it is shown that the mean free path of the anion is proportional to its rotational volume. Over the second range the fall in conductivity is extremely rapid. The anionic network postulated offers a satisfactory explanation and is in accordance with other properties observed over this range. At the point where the second range is succeeded by the third it is shown that the distance between the anions in the network is proportional to their length. In any homologous series the tendency to form micelle is proportional to the length of the anion. This is the point, therefore, at which the network falls into micelle formation. In our observations the curves that have been drawn are similar to the second and third regions of the curves found by Howell and Robinson. In most of the cases the fall in conductivity is extremely rapid and is followed by a region where the conductivity either rises to maximum or remains practically constant. At the point where the second range is succeeded by the third the network falls into micelle formation.

In the alcoholic solution also there is no perfect linear relationship between the molecular conductivity and square root of concentration and the conductivity-

concentration curves are similar to those for aqueous solution. The difference in the behaviour of dyestuffs in these two solvents may be due to different degree of aggregation of ions. It has been shown by Mitra that quenching co-efficients of dyestuffs in alcoholic solution are distinctly less than in aqueous solution which also supplies evidence as to the low association in alcoholic-solution.

It is interesting to note that the critical concentration at which the network falls into ionic micelles fairly coincides with the concentration after which rapid quenching of fluorescence begins. It, therefore, supports the view that the quenching of fluorescence is due to the formation of ionic micelles.

Influence of foreign substances on the conductivity of the dyestuffs : It is well known that the addition of small quantities of a foreign substance to a fluorescent solution causes a quenching of its fluorescent radiation with a simultaneous diminution of its efficiency. This phenomenon of the quenching of the fluorescence of the dye solution has been investigated by a number of workers and some of them are at present inclined to the view that the quenching effect is due to the deactivation of the excited molecule with a molecule of the foreign substance through collision of the second kind. The principal argument in the favour of this physical interpretation of the quenching effect is the increase of polarisation by quenching, which was first observed by Mitra in the case of dyestuffs.

In our present investigations we have also investigated the influence of the foreign molecule or ions on the conductivity of the fluorescent compounds in solution. The results of our measurements are shown in the following tables.

TABLE VII

Eosin and Potassium Iodide

0.1597 gms of eosin was taken in 35 c.c. of water and that corresponds to 1/4 C solution. 30 c.c. of the solution was taken in the conductivity cell.

Vol. in cc. of N-KI soln. added	Strength of KI solution in the mixt.	Sp. conduct. of the KI solution K_1	Strength of eosin soln. in the mixt.	Sp. cond. of the eosin soln. K_2	$K_1 + K_2$	Observed sp. conductivity.
0	0	0	C	.001444	.001444	.001444
.5	1/61 N	.002611	1/4.075C	.001440	.004051	.004084
1.0	1/31 N	.005021	1/4.12C	.001396	.006417	.006542
2.0	1/16 N	.009376	1/4.26C	.001350	.010726	.01062
4.0	1/8.5 N	.01713	1/4.53C	.001265	.018395	.01847
8.0	1/4.75 N	.02989	1/5.07C	.001119	.031009	.03028
12.0	1/3.5 N	.03868	1/5.6C	.001000	.03968	.04055

TABLE VIII

Erythrosin and Potassium iodide

.3499 gms. of erythrosin was taken in 50 c.c. of water and that corresponds to 1/16C solution. 30 c.c. of the solution was taken in the conductivity cell.

Volume in c.c. of N-KI soln. added	Strength of KI solution in the mixt.	Sp. conduct. of KI soln. K_1	Strength of erythrosin soln. in the mixture	Sp. conduct. of erythrosin soln. K_2	$K_1 + K_2$	Observed sp. conductivity
0	0	0	C/16	.005540	.005540	.005540
.5	1/61 N	.002611	C/16.3	.005461	.008072	.008035
1.0	1/31 N	.005021	C/16.48	.005406	.01043	.01026
2.0	1/16 N	.009376	C/17.04	.005226	.01460	.01423
4.0	1/8.5 N	.01713	C/18.12	.004639	.02176	.02047
8.0	1/4.75 N	.02989	C/20.28	.004072	.03396	.03160
12.0	1/3.5 N	.03868	C/22.4	.003658	.04233	.04083

It will be seen from the tables that the conductivity of the solution is very nearly equal to the sum of the individual conductivities of the dyes and potassium iodide in solution. This shows that no new molecules are formed due to the gradual addition of potassium iodide and that the collision of the second kind is the major cause of quenching by foreign neutral salts. Our measurements are in agreement with those of Mitra and others.

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